




Original document

**ALUMINA-BASED CERAMIC SINTERED COMPACT**

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**Abstract of JP7277814**

**PURPOSE:**To produce an alumina-based ceramic sintered compact having high strength and high toughness and hardly reducing its strength even at high temp. (1,200 deg.C). **CONSTITUTION:**A l having a chemical compsn. consisting of 1-10wt.% La<sub>2</sub>O<sub>3</sub>, 0.01-0.1wt.% SiO<sub>2</sub> and the balance Al<sub>2</sub>O<sub>3</sub> is compacted and held under heating in the temp. range of 1,400-1,800 deg.C so that the resultant sintered compact is densified to  $\geq 95\%$  relative density and the crystal phase of the sintered compact is composed of corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and lanthanum.beta-alumina (La<sub>2</sub>O<sub>3</sub>.11 Al<sub>2</sub>O<sub>3</sub>). The object of the invention is to provide an alumina-based ceramic sintered compact having high strength and high toughness and capable of exhibiting high strength at high temp. is obtd.

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This invention relates to a sintered ceramic article formed mainly of alumina and has particular reference to a sintered ceramic which is characterized by exhibiting high toughness at normal room temperature and at elevated temperatures (1200 DEG C). This invention also includes a method for the production of a sintered ceramic article.

Alumina has a high melting point, is thermally stable, and excels in resistance to abrasion, insulation property, and resistance to corrosion and, on account of these features, has found extensive utility as an industrial material. For example, the high electric insulating property of alumina is utilized in electric components such as spark plugs, IC substrates, and packages as well as in light-pervious alumina, bioceram and other such highly functional sintered articles and single-crystal materials. Practical application of alumina as a functional material has thus been extended into a wide range of fields. Application of alumina as a structural material, however, has been slower. This can be traced to the low toughness of alumina, which is in the range of 3 to 4 MPam<sup>1/2</sup>. In terms of resistance to oxidation and corrosion, however, alumina is fundamentally superior to such non-oxide ceramic materials as silico

nitride and silicon carbide which are the main ceramic structural materials in use today. It is therefore regarded as a potentially excellent structural material. Moreover, alumina can be fired in the open air whereas the non-oxide ceramic materials are required to be fired in nitrogen, argon or other such non-oxidizing gas atmosphere. A plant for the production of sintered alumina articles is therefore not very expensive to construct. Further, it can be operated at a low running cost.

Various methods have been studied for improving the toughness of alumina. These methods can be roughly divided into the four types: (1) dispersion of  $ZrO_2$ , (2) dispersion of platelike particles or whiskers, (3) growth of platelike alumina particles by the addition of a liquid phase forming auxiliary (4) the growth of platelike particles as  $La_2O_3 \cdot 11Al_2O_3$  (hereinafter referred to briefly as " $LaAl_{11}O$ ") a coexistent relationship with alumina. The method of (1) consists in utilizing the stress-induced modification of zirconia. It is reported that the alumina produced by this method possesses a high fracture toughness in the range of from 5 to 8 MPa $\sqrt{m}$ . Since the mechanism for increasing toughness utilizes the phase modification of zirconia, high toughness can be obtained by this mechanism only at temperatures not exceeding the temperature of the monoclinic system-tetragonal system modification of zirconia (800 DEG C).

The method of (2) consists in dispersing in alumina from 10 to 30% by volume, based on alumina, of whiskers or platelike particles of a non-oxide material with form anisotropy such as silicon carbide or silicon nitride. The toughness of alumina is enhanced by causing the dispersed whiskers or platelike particles to produce a bridging or a fiber extracting effect along edges of cracks produced by grain boundary breaking. As reported in J. Am. Ceram. Soc., 67 [12], C267-C269 (1984), this method produces a sintered article with a high fracture toughness on the order of 8.7 MPa $\sqrt{m}$ . On the other hand, however, the strength of the sintered article is reduced because the added platelike particles or whiskers function as faults. Besides, since the method requires a large amount of these platelike particles or whiskers to be dispersed, namely as much as 10 to 30% by volume based on alumina, the reinforced alumina must be fired by hot pressing or hot isostatic pressing (HIP). This method is therefore very expensive and is not applicable for obtaining a sintered article of complicated shape. Further, since a non-oxide ceramic material such as silicon carbide or silicon nitride is used as a dispersing material, it is likely that the reinforced alumina will deteriorate and lose its fortified toughness by oxidation at elevated temperatures and the product of this method will not endure protracted use either at elevated temperatures or in a corrosive environment. The method of (3), as reported in Mater. Sci., 28, 5953-56 (1993), for example, consists in using silica-calcia, silica-magnesia or other such firing material which reacts with alumina in the firing temperature range and forms a liquid phase, thereby enabling the alumina particles to grow during firing into plates of high anisotropy and consequently increasing the toughness by a mechanism similar to that obtained by the addition of platelike particles. This method, however, has the disadvantage that the sintered article experiences a marked decrease in strength at high temperatures because a low-melting vitreous phase persists in the sinter. The method of (4) consists in causing platelike hexaaluminate particles (such as  $LaAl_{11}O_{18}$  and  $LaMgAl_{11}O_{18}$ ) to grow in an alumina matrix during sintering. The product of this method suffers only a slight decline of mechanical properties because no low-melting vitreous phase persists in the sinter. As reported in J. Am. Ceram. Soc., 75 [9], 2610-12 (1992), the fracture toughness of this product is about 4 MPa $\sqrt{m}$ . Thus, this method gives only a small increase in toughness.

From the foregoing it is obvious that the prior art methods are incapable of producing a sintered alumina article having both high strength and high toughness at temperatures ranging from normal room temperature to elevated temperatures under various circumstances including corrosive environments.

An object of this invention is to provide a sintered article formed mainly of alumina which exhibits high strength and high toughness at temperatures ranging from room temperature to elevated temperatures in corrosive environments and which enables easy fabrication of products even in complicated shapes by a simple process at a low cost.

Another object of the invention is to provide a method for the production of the sintered article.

According to one aspect of the present invention therefore there is provided a sintered ceramic article comprising alumina, characterised by the incorporation of  $\text{LaAl}_{11}\text{O}_{18}$  in the alumina matrix and an amount of silica such that the  $\text{LaAl}_{11}\text{O}_{18}$  and alumina matrix comprise platelike particles.

The inventors noted that  $\text{LaAl}_{11}\text{O}_{18}$  has excellent resistance to heat and, when incorporated in an aluminum matrix and sintered, grows in the form of platelike particles. Based on this finding, they in study with a view to developing a method for utilizing  $\text{LaAl}_{11}\text{O}_{18}$  to produce a sintered article formed mainly of alumina and exhibiting enhanced toughness. In the early stage of their study, they found that a sintered article obtained by firing a shaped piece of a mixture of  $\text{Al}_2\text{O}_3$  with  $\text{La}_2\text{O}_3$  shows no substantial improvement in toughness because the alumina particles constituting the matrix assume an isometric form whereas the compound  $\text{LaAl}_{11}\text{O}_{18}$  formed by the reaction of the starting raw materials grows in the form of platelike particles. They continued their study of the system based on this knowledge and consequently found that addition of a very small amount of silica allows the  $\text{LaAl}_{11}\text{O}_{18}$  to retain its platelike particle form and, at the same time, enables the alumina constituting the matrix to assume the form of platelike particles and, owing to the combined particle-forming effects of the two compounds, enables production of a material having higher toughness than the conventional  $\text{Al}_2\text{O}_3$ - $\text{LaAl}_{11}\text{O}_{18}$  type material. They further found that this addition of a very small amount of silica has virtually no adverse effect on the high-temperature strength of the sintered article produced.

The invention may concern a sintered ceramic article formed mainly of alumina, having a chemical composition of from 1 to 10% by weight of  $\text{La}_2\text{O}_3$ , from 0.01 to 0.1% by weight of  $\text{SiO}_2$ , and the balance of  $\text{Al}_2\text{O}_3$ . The article may substantially comprise corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) and lanthanum beta-alumina ( $\text{La}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$ ). The invention also includes a method for the production of the sintered ceramic article formed mainly of alumina by shaping a mixture of  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ , and  $\text{SiO}_2$ , calcining the shaped mixture in the air at a temperature in the range of from 600 DEG C to 1000 DEG C, and further firing the calcined mixture to a temperature in the range of from 1400 DEG C to 1800 DEG C.

The sintered ceramic article of this invention may also be characterised by being densified to a relative density of not less than 97%.

In a different aspect of the invention there is provided a method for the production of a sintered alumina-based ceramic article comprising sintering a mixture containing alumina, characterized in that said mixture incorporates  $\text{LaAl}_{11}\text{O}_{18}$  in the alumina matrix and an amount of silica such that the  $\text{LaAl}_{11}\text{O}_{18}$  and alumina form platelike particles. Typically the invention comprises shaping a mixture having a chemical composition of from 1 to 10% by weight of  $\text{La}_2\text{O}_3$ , from 0.01 to 0.1% by weight of  $\text{SiO}_2$ , and the balance of  $\text{Al}_2\text{O}_3$  and subsequently firing the shaped mixture. The mixture may be fired at a temperature in the range of from 1400 DEG C to 1800 DEG C thereby densifying the texture thereof to a relative density not less than 97% and a sintered alumina-based ceramic article characterized in that its crystal phase comprises corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) and lanthanum beta-alumina ( $\text{La}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$ ).

As the first step in the production of the sintered article formed mainly of alumina according to this invention, a mixture having a chemical composition of from 1 to 10% by weight of  $\text{La}_2\text{O}_3$ , from 0.01 to 0.1% by weight of  $\text{SiO}_2$ , and the balance of  $\text{Al}_2\text{O}_3$  is prepared.

The  $\text{La}_2\text{O}_3$  content of this mixture is in the range of from 1 to 10% by weight, preferably from 3 to 10% by weight. If the content is less than 1% by weight, the sintered article produced will acquire a low fracture toughness of not more than 5 MPa $\sqrt{\text{m}}$  because the platelike particles of  $\text{LaAl}_{11}\text{O}_{18}$  are produced in only a small amount. Conversely, if the content exceeds 10% by weight, the sintered article produced will have low strength because the formed  $\text{LaAl}_{11}\text{O}_{18}$  will account for not less than 40% of the sintered article by volume, the sintering will occur among the adjacent  $\text{LaAl}_{11}\text{O}_{18}$  particles, and the sintered article produced will acquire properties which approximate those of  $\text{LaAl}_{11}\text{O}_{18}$ . It is, therefore, important to confine the content within the range specified above.

The silica content of the mixture is in the range of from 0.01 to 0.1% by weight, preferably from 0.01 to 0.08% by weight. If the content is less than 0.01% by weight, the sintered article produced will have

fracture toughness because the alumina constituting the matrix will fail to attain full growth into plate particles. Conversely, if the content exceeds 0.1% by weight, the sintered article produced will show signs of lowered high-temperature strength because the amount of vitreous phase originating in the liquid phase formed in the process of sintering and remaining among the sinter particles will increase. It is, therefore, important to confine the content within the range mentioned above.

For the preparation of the mixture, either powdery compounds of  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{LaAlO}_3$ , and  $\text{SiO}_2$  precursor compounds which yield such oxides when heated are used as the starting materials. As the one which constitutes a trace component of the mixture, it is advantageous to use silicon alkoxides like tetraethyl silicate and colloidal silica in view of their amenability to homogeneous mixing. As the source for alumina and lanthanum oxide, powdery materials are generally used. As the source for lanthanum oxide, it is particularly desirable to use  $\text{LaAlO}_3$  powder. This is because  $\text{La}_2\text{O}_3$  reacts readily with water and, when persisting in its unaltered form in the mixture, absorbs moisture to cause swelling of the mixture. The raw materials, namely  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{LaAlO}_3$ ,  $\text{SiO}_2$ , etc. should best have a high purity not less than 99.9%.

For mixing these raw materials, any of the conventional machines used for mixing or kneading powdery materials can be used. Though this mixing may be carried out in a wet or a dry process, it is desirably performed in the wet process. In the wet mixing, such solvents as water, methanol, ethanol, and toluene are usable. The mixing can be carried out effectively in water by adjusting the pH of the mixture in the range of from 3 to 5 as by dropwise addition of nitric acid and in an organic solvent by using such a dispersant as cationic cellulose. Further, in the mixing or kneading process, it is desirable to exercise such precautions as using balls made of high-purity alumina as a pulverizing medium and a container made of high-purity alumina or synthetic resin as a mixing vessel so that the amount of the impurities which pass from the balls and the vessel into the produced mixture and cannot be removed by heating can be limited to below 50 ppm by weight.

This invention specifies use of raw materials of high purity and recommends use of balls made of high-purity alumina and a container made of high-purity alumina or synthetic resin in the process of mixing these raw materials in order to preclude the possibility that such impurities as alkali metals and alkaline earth metals entering the raw materials prior to or during the firing process will form a low-melting vitreous phase and markedly degrade the high-temperature properties of the sintered article produced. Commercially available high-purity alumina and lanthanum oxide raw materials generally contain silica at the rate of some tens of ppm. When such commercially available materials are used, therefore, it is desirable to keep the silica content of the mixture below 0.005% by weight (50 ppm), especially when additional silica is present at the site of the mixing process. It is, therefore, desirable to measure the amount of silica from the mixing environment before hand, as by emission plasma spectroanalysis, and then adjust the amount of silica to be added during the preparation of the mixture.

Then, the mixture of raw materials obtained as described above is formed into a desired shape by a compression or filter press wet molding technique or by provisionally drying the mixture by the spray dry technique, for example, and then dry molding the dried mixture by the conventional drying technique.

Subsequently, the shaped mixture is fired by the conventional firing method which comprises first calcining the mixture in the air at a temperature in the approximate range of from 600 DEG C to 1000 DEG C thereby thermally removing therefrom such extraneous substances as salts, dispersant, and residual moisture admitted in the mixing process and thereafter firing the calcined mixture at a temperature in the range from 1400 DEG C to 1800 DEG C, preferably from 1500 DEG C to 1700 DEG C, thereby densifying. For the purpose of realizing high strength and high toughness in this case, it is necessary that the mixture be densified to a relative density of not less than 97% and the reaction between the raw materials be allowed to proceed thoroughly until the sintered article forms a crystal phase consisting solely of  $\text{Al}_2\text{O}_3$  and  $\text{LaAl}_{11}\text{O}_{18}$ . If the firing temperature is less than 1400 DEG C, the sintered article produced will acquire low fracture toughness because the mixture cannot be densified to a relative density exceeding 97%, residual pores will be a possible cause of rupture and bring about a decrease of strength, and the plate crystals of  $\text{LaAl}_{11}\text{O}_{18}$  will not be sufficiently formed. Conversely, if the firing temperature exceeds

DEG C, the particles of  $\text{Al}_2\text{O}_3$  and  $\text{LaAl}_{11}\text{O}_{18}$  will grow excessively to the extent of lowering strength. Thus, it is necessary that the firing be carried out in the temperature range mentioned above. Further relationship between the firing time and the firing temperature is such that the firing time should be lengthened when the firing temperature is low and shortened when the firing temperature is high. For purpose of meeting the conditions mentioned above and realizing high strength and high toughness, however, it is advisable to carry out the densification for a period in the range of from 0.1 to 10 hours. The sintered article is characterized by the fact that the densification can be attained by ordinary pressure which is easy to perform. Alternatively, the densification may be effected by hot pressing or HIP, for example.

Although an oxidative atmosphere is preferably used in the firing process, it is also allowable to carry out the firing process in a non-oxidative atmosphere (nitrogen gas or argon gas).

The sintered ceramic article of this invention obtained as described above and formed mainly of alumina possesses a microstructure having platelike lanthanum beta -alumina particles dispersed in an alumina matrix formed of platelike particles. The microstructure having such intermixed platelike particles produces high toughness. Further, the different sorts of platelike particles dispersed in the microstructure mutually repress their abnormal grain growth, uniformize distribution of particle sizes, increase strength, do not permit persistence of any low-melting substance after sintering, and consequently promote high-temperature strength. This invention is therefore capable of producing a sintered ceramic article formed mainly of alumina and exhibiting such heretofore unattainable properties as high strength, high toughness and high strength at elevated temperatures.

Prior to completing the invention, the inventors found that by the sole addition of a very small amount of  $\text{SiO}_2$  to alumina, the particles of alumina which are in an isometric form in the absence of this additive grow in a platelike form. They also ascertained that the sintered article obtained from the mixture involving the sole addition of  $\text{SiO}_2$  acquires an extremely heterogeneous texture having giant platelike alumina particles and minute platelike alumina particles mixed therein and, as a result, exhibits rather lower strength and fracture toughness than the sinter excluding the addition of  $\text{SiO}_2$ , as shown in Table 1 appearing later in this specification. Further, in the mixture involving the sole addition of  $\text{La}_2\text{O}_3$ , the improvement in the toughness of the sintered article is slight. This invention is characterized by the fact that high strength and high toughness unattainable by the sole addition of  $\text{SiO}_2$  or  $\text{La}_2\text{O}_3$  can be attained by simultaneous addition of  $\text{SiO}_2$  and  $\text{La}_2\text{O}_3$ .

As clearly shown in Table 1, which summarizes the results obtained in the working examples and comparative examples described hereinbelow, when the raw materials fall in the content ranges specified by this invention, the sintered article produced assumes a crystal phase consisting of  $\text{Al}_2\text{O}_3$  and  $\text{LaAl}_{11}\text{O}_{18}$  and exhibits room temperature strength of not less than 500 MPa, high-temperature (1200 DEG C) strength of not less than 350 MPa, and fracture toughness of not less than 5  $\text{MPa}\cdot\text{m}^{1/2}$ .

This invention thus provides a sintered ceramic article which is formed mainly of alumina and exhibits high strength, high-temperature strength, and high toughness on a high level not attainable by the conventional sintered ceramic article formed mainly of alumina.

The sintered ceramic article according to this invention, which is formed mainly of alumina, can then be expected to find extensive utility as a structural material for use in corrosive environments which are endured by conventional materials. It can also be expected to be adopted as an inexpensive high-temperature structural material for use in the place of refractory alloys and non-oxide ceramic materials. Specifically, the sintered ceramic article can be used in pumps, seals, nozzles, bearings and other mechanical components which require resistance to corrosion and resistance to abrasion, and also in heat exchangers, engines, gas turbine components and other products which require resistance to heat. Further, in the field of electronic material parts, bioceramics and other functional materials, the sintered ceramic article of this invention can be expected to dramatically improve material reliability through increase in toughness.

The invention will now be described specifically below with reference to working examples and comparative examples.

#### EXAMPLES 1 TO 7 AND COMPARATIVE EXAMPLES 1 TO 7

The procedures involved in these working examples and the comparative examples were identical except that the raw material powders used therein were varied in composition.

The procedure used was as follows.

A liquid silica dispersion was prepared by adding 250  $\mu$ l of 1N nitric acid to a prescribed amount of tetraethyl silicate and stirring them together at 40 DEG C for 12 hours to make hydrolysis. In a planetary ball mill using balls made of high-purity alumina with an assay of 99.9% and a mixing vessel made of plastic resin, 32 cc of distilled water, the whole amount of the liquid silica dispersion and prescribed amounts of  $Al_2O_3$  powder and  $LaAlO_3$  powder in the distilled water, and 2.5 cc of 1N nitric acid added thereto were together mixed for two hours. The  $Al_2O_3$  powder had a purity of not less than 99.99%, a particle diameter of 0.2  $\mu$ m and the  $LaAlO_3$  powder had a purity of not less than 99.9% and a particle diameter of 0.5  $\mu$ m. The total amount of these powders was about 70 g. The prescribed amounts mentioned above were such that the raw material compositions of the working examples and the comparative examples had the numerical values shown in Table 1 below. The raw material contents in the working examples and the comparative examples are also shown in the table. The slurry consequently obtained was cast molded under a pressure of 4 kg/cm<sup>2</sup> to obtain a shaped plate measuring 60 x 50 x 7 mm. This shaped plate was dried for twenty-four hours in a constant temperature-constant humidity bath kept at a temperature of 50 DEG C and 50% RH. Then, it was calcined in the air at 800 DEG C for one hour to remove salts and the resin leaked from the mixing vessel. A sintered article was obtained by setting the calcined plate in an alumina crucible, heating it in the air at a temperature increasing rate of 10 DEG C/min to 1600 DEG C, and leaving it to stand at 1600 DEG C for two hours. The sintered article thus obtained was cut into test pieces measuring 3 x 4 x 40 mm. The test pieces were ground, tested for four-point bending strength at room temperature in accordance with Japanese Industrial Standard (JIS) R-1601, for high-temperature four-point bending strength at 1200 DEG C in accordance with JIS R-1604, and for fracture toughness by the SEPB method according to JIS R-1607. In consideration of the possible entry of impurities, particularly silica, during the mixing, forming, and processes of the mixture, the chemical composition of the sinter was determined by the emission plasma spectroanalysis (ICP method). The chemical analysis according to the ICP method revealed no other cationic impurities than Al, La, and Si. The results of the determination of mechanical properties, chemical composition, densities, and crystal phases for X-ray diffraction are shown in Table 1 together with the raw material contents. The numerical values of density shown in the table represent the magnitudes of relative density (%) based on theoretical density. EMI15.1

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Claims of corresponding document: **EP0659705**

1. A sintered ceramic article formed mainly of alumina, having a chemical composition of from 1 to 100% by weight of  $La_2O_3$ , from 0.01 to 0.1% by weight of  $SiO_2$ , and the balance of  $Al_2O_3$ , and substantially comprising corundum ( $\alpha$ - $Al_2O_3$ ) and lanthanum beta-alumina ( $La_2O_3 \cdot 11Al_2O_3$ ).

2. A sintered ceramic article according to claim 1, wherein the content of said  $La_2O_3$  is in the range of from 3 to 7% by weight.

3. A sintered ceramic article according to claim 1, wherein the content of said  $SiO_2$  is in the range of from 0.01 to 0.1% by weight.

0.02 to 0.08% by weight.

4. A method for the production of a sintered ceramic article formed mainly of the alumina, which comprises shaping a mixture of  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ , and  $\text{SiO}_2$ , calcining the shaped mixture in the air at a temperature in the range of from 600 DEG C to 1000 DEG C, and further firing the calcined shaped mixture to a temperature in the range of from 1400 DEG C to 1800 DEG C.

5. A method according to claim 4, wherein said mixture comprises from 1 to 10% by weight of  $\text{La}_2\text{O}_3$  from 0.01 to 0.1% by weight of  $\text{SiO}_2$ , and the balance of  $\text{Al}_2\text{O}_3$ .

6. A method according to claim 4, wherein said firing is performed at a temperature in the range of from 1500 DEG C to 1700 DEG C.

7. A method according to claim 5, wherein the content of said  $\text{La}_2\text{O}_3$  is in the range of from 3 to 7% by weight.

8. A method according to claim 5, wherein the content of said  $\text{SiO}_2$  is in the range of from 0.02 to 0.1% by weight.

9. A method according to claim 4, wherein the heating temperature for said firing is maintained for a period in the range of from 0.1 to 10 hours after the completion of said firing.

10. A method of producing a sintered ceramic articles comprising sintering a mixture containing alumina, characterised in that said mixture incorporates  $\text{LaAlSiO}_8$  in an alumina matrix and an amount of silica such that the alumina and  $\text{LaAlSiO}_8$  form platelike particles.

11. A sintered ceramic article comprising alumina, characterised in that the alumina matrix comprises  $\text{LaAlSiO}_8$  and an amount of silica such that the alumina and  $\text{LaAlSiO}_8$  comprise platelike particles.

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(54) 【発明の名称】 アルミナ基セラミックス焼結体

(57) 【要約】

【目的】 高強度、高靱性でかつ高温(1200℃)においても強度低下の少ないアルミナ基セラミックス焼結体を提供する。

【構成】  $\text{La}_2\text{O}_3$  が1~10重量%、 $\text{SiO}_2$  が0.01~0.1重量%、残りが $\text{Al}_2\text{O}_3$  からなる化学組成を有する配合物を成形後、1400~1800℃の温度域で加熱保持し、該焼結体の相対密度が95%以上に緻密化され、かつ該焼結体の結晶相がコランダム( $\alpha\text{-Al}_2\text{O}_3$ )とランタンβ-アルミナ( $\text{La}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$ )から構成されることにより、高強度、高靱性、ならびに高温高強度の発現を可能としたアルミナ基セラミックス焼結体及びその製造方法。

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## 【特許請求の範囲】

【請求項1】  $\text{La}_2\text{O}_3$  が1~10重量%、 $\text{SiO}_2$  が0.01~0.1重量%、残りが  $\text{Al}_2\text{O}_3$  からなる化学組成を有し、かつ焼結体を構成する結晶相がコランダム ( $\alpha\text{-Al}_2\text{O}_3$ ) とランタン $\beta$ -アルミナ ( $\text{La}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$ ) からなることを特徴とするアルミナ基セラミックス焼結体。

【請求項2】  $\text{Al}_2\text{O}_3$ 、 $\text{La}_2\text{O}_3$ 、 $\text{SiO}_2$  よりなる配合物を成形後、1400~1800℃の温度域で焼成することにより相対密度97%以上に緻密化することを特徴とする請求項1に記載のアルミナ基セラミックス焼結体の製造方法。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明はアルミナを主体とし、常温および高温(1200℃)における高強度と高靱性の同時発現を可能とする、アルミナ基セラミックス焼結体に関するものである。

【0002】

【従来の技術】 アルミナは融点が高く熱的にも安定であり、さらに耐摩耗性、絶縁性、耐食性等に優れることから、工業材料として幅広い分野で利用されている。例えば、その高い電気絶縁性を利用して、スパークプラグ、IC基板、パッケージ等の電子材料部品として、さらに透光性アルミナ、バイオセラムなどの高機能性焼結体や単結晶材料として使用されている。このように機能性材料としてのアルミナは実用材料として既に広い分野で利用されているが、構造材料としての利用はこれら機能性材料の場合と比較して遅れているのが現状である。これはアルミナ焼結体の靱性が3~4MPa $\text{m}^{1/2}$ と低いことに原因している。しかし、アルミナは現在セラミックス系構造材料の主流である窒化ケイ素、炭化ケイ素等の非酸化物セラミック材料と比較して本質的に耐酸化性、耐食性に優れており、潜在的に優れた構造材料と考えられる。さらに、非酸化物セラミックス材料の製造においては窒素、アルゴン等非酸化性雰囲気中での焼成が必要であるのに対し、アルミナは設備投資並びにランニングコストが兼価である大気中での焼成が可能であるという利点を有している。

【0003】 そこでアルミナの靱性を改善するため現在まで種々の方法が検討されてきた。これらの方法は作製手法及び靱性強化機構の観点から、(1)  $\text{ZrO}_2$  分散、(2) 板状粒子あるいはウィスカー分散、(3) 液相生成助剤添加による板状アルミナの成長、(4) アルミナと共存関係にある  $\text{La}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$  (以降  $\text{LaAl}_{11}\text{O}_{19}$  と略記する) などの板状粒子の成長に分類される。(1)の方法はジルコニアの応力誘起変態を利用するもので5~8MPa $\text{m}^{1/2}$ と高い破壊靱性が報告されている。しかし、その靱性強化機構はジルコニアの単斜晶-正方晶の変態温度(400~800℃)以下の温度に限られる。

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(2)は形状異方性を持つウィスカーや板状粒子によるキ裂縁での架橋あるいは引き抜け効果により靱性向上を図る方法である。この手法においても、例えば、J. Am. Ceram. Soc., 67 [12] C267-C269 (1984)に報告されているように、8.7MPa $\text{m}^{1/2}$ と高い破壊靱性を持つ焼結体を得られているが、添加した強化材が欠陥として作用するため焼結体の強度は低下する。加えて、10~30体積%の異種材料を分散させるために、ホットプレス法や熱間加圧成形法(HIP)で焼成を行わねばならず、プロセスが高価でありかつ複雑な形状を有する焼結体を得ることは困難である。また、これら分散材料としては炭化ケイ素、窒化ケイ素等非酸化物が用いられるため、高温において酸化による劣化を生じ靱性強化の効果を損ない、高温下あるいは腐食環境下での長時間の使用には耐えられないと考えられる。(3)の方法は、例えば、J. Mater. Sci., 28 5953-56 (1993)に報告されているように、シリカーカルシア、シリカ-マグネシア等の焼成温度域でアルミナと反応して液相を生成する焼成助剤を用いることにより、焼結時にアルミナ粒子を異方性の高い板状に成長させ、板状粒子添加と同様な機構により靱性強化を図るものである。しかし、この手法では焼結体中に低融点のガラス相が残留するため、高温での強度低下が著しいという欠点を有する。(4)はアルミナマトリックス中に板状のヘキサアルミネート粒子( $\text{LaAl}_{11}\text{O}_{19}$ 、 $\text{LaMgAl}_{11}\text{O}_{19}$ 等)を焼結時に成長させる手法で、焼結体中に低融点ガラス相が残留しないため高温での機械的特性の低下が小さいが、その破壊靱性は例えばJ. Am. Ceram. Soc., 75 [9] 2610-12 (1992)に報告されているように4MPa $\text{m}^{1/2}$ 程度であり、靱性向上レベルは小さい。

【0004】

【発明が解決しようとする課題】 上述したように、従来の靱性強化手法で得られた焼結体は、常温から高温あるいは腐食雰囲気に至る環境下で高強度及び高靱性を同時に維持することが困難であり、アルミナの構造材料としての潜在能力を十分に発揮させるものではなかった。

【0005】 本発明の目的は、常温から高温あるいは腐食環境下において高強度、高靱性を有し、かつプロセスが兼価で複雑形状への適用が容易なアルミナ基焼結体及びその製造方法を提供することにある。

【0006】

【課題を解決するための手段】 発明者らは、 $\text{LaAl}_{11}\text{O}_{19}$ が耐熱性に優れ、しかもアルミナマトリックス中に焼結時に板状粒子として成長させられることに注目し、 $\text{Al}_2\text{O}_3$ - $\text{LaAl}_{11}\text{O}_{19}$ 系組成を中心にアルミナ基焼結体の靱性強化について鋭意研究を行った。その結果、 $\text{Al}_2\text{O}_3$ と $\text{La}_2\text{O}_3$ の混合物からなる成形体を焼成して得られた焼結体においては、出発原料間の反応で生成する $\text{LaAl}_{11}\text{O}_{19}$ は板状に成長するもののマトリックスのアルミナ粒子は等軸状であり、このことが本系において靱性の向上レベルの

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低下の要因であることが分った。この知見を基にさらに本系について研究を進めた結果、極微量のシリカ添加により $\text{LaAl}_{11}\text{O}_{18}$ の板状粒子形態を維持しつつ、マトリックスのアルミナについても板状粒子化が達成され、両者の粒子形状効果が合わさり従来の $\text{Al}_2\text{O}_3$ - $\text{LaAl}_{11}\text{O}_{18}$ 系材料と比較してより靱性の高い材料が得られること、及び極微量のシリカ添加は高温強度にほとんど影響を及ぼさないことを見だし、以下に示す要旨構成の本発明に至った。

【0007】すなわち、本発明は、 $\text{La}_2\text{O}_3$ が1~10重量%、 $\text{SiO}_2$ が0.01~0.1重量%、残りがアルミナから成る化学組成を有する配合物を成形後、1400~1800℃で焼成することにより相対密度97%以上に緻密化することを特徴とするアルミナ基セラミックス焼結体の製造方法と、それによって得られる焼結体の結晶相がコランダム( $\alpha$ - $\text{Al}_2\text{O}_3$ )とランタン $\beta$ -アルミナ( $\text{La}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3$ )からなることを特徴とするアルミナ基セラミックス焼結体である。

【0008】本発明のアルミナ基焼結体を得るには、まず、 $\text{La}_2\text{O}_3$ が1~10重量%、 $\text{SiO}_2$ が0.01~0.1重量%、残りがアルミナからなる化学組成を有する配合物を作製する。

【0009】ここで、 $\text{La}_2\text{O}_3$ 含有量に関しては、1~10重量%の範囲、好ましくは3~7重量%の範囲である。そしてその量が1重量%以下では、板状 $\text{LaAl}_{11}\text{O}_{18}$ 粒子の生成量が少ないため焼結体の破壊靱性が5MPa $\text{m}^{1/2}$ 以下と低くなる。一方、その量が10重量%以上では、生成する $\text{LaAl}_{11}\text{O}_{18}$ の体積割合が40体積%以上となり、 $\text{LaAl}_{11}\text{O}_{18}$ 粒子間で焼結が生じ、得られる焼結体の特性が $\text{LaAl}_{11}\text{O}_{18}$ の特性に近いものとなるため強度低下などをもたらすので、上記範囲に制限することが重要である。

【0010】また、シリカの含有量に関しては、0.01~0.1重量%の範囲、好ましくは0.02~0.08重量%の範囲である。そしてその量が0.01重量%以下では、マトリックスであるアルミナが十分に板状に成長しないため焼結体の破壊靱性は低くなる。一方、その量が0.1重量%以上では、焼結時に生成する液相に起因した粒子間に残存するガラス相の量が増大し、高温強度の低下が顕著に生じる。したがって、上記組成に制限することが重要である。

【0011】配合物の作製において、出発原料として $\text{Al}_2\text{O}_3$ 、 $\text{La}_2\text{O}_3$ 、 $\text{LaAlO}_3$ 、 $\text{SiO}_2$ などの粉末原料あるいは加熱時にこれら酸化物を誘導する前駆体化合物が用いられる。特に、微量成分であるシリカに関しては均一な混合を達成するために、テトラエチルシリケートなどのシリコン-アルコキシドやコロイダルシリカが好適に用いられる。また、アルミナ及び酸化ランタン源としては粉末原料が一般に使用されるが、特に酸化ランタン源としては $\text{LaAlO}_3$ 粉末を用いることが好ましい。これは $\text{La}_2\text{O}_3$ は

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水分と反応し易く、 $\text{La}_2\text{O}_3$ として配合物に存在した場合、吸湿により成形体が膨潤するからである。さらに、使用するこれら原料に関しては、 $\text{Al}_2\text{O}_3$ 、 $\text{La}_2\text{O}_3$ 、 $\text{LaAlO}_3$ 、 $\text{SiO}_2$ などいずれも純度99.9%以上の高純度原料を使用することが望ましい。

【0012】また、これら原料の混合に当たっては、粉体の混合あるいは混練に用いられる通常の機械を使用することができる。この混合は、湿式、乾式のどちらでもよいが、望ましくは湿式において混合される。湿式混合においては、水、メタノール、エタノール、トルエンなどの溶剤が用いられる。水中での混合においては硝酸などを滴下しpHを3~5に調整することにより、また有機溶剤を用いた場合はカチオン性セルロースなどの分散剤を用いることにより効果的に混合を行うことができる。さらに、混合あるいは混練過程においては、粉砕メディアとして高純度アルミナ製ボール、混合容器として高純度アルミナ製あるいは樹脂製容器を用いるなどして、本工程においてボール、容器から混入する加熱除去が困難な不純物を0.1重量%以下にすることが望ましい。

【0013】本発明において、高純度原料を使用し、さらにその混合工程において高純度アルミナ製ボール、高純度アルミナ製容器、樹脂製容器などを用いる理由は、原料およびその焼成工程時において混入するアルカリ金属、アルカリ土類金属などの不純物が焼成時に低融点のガラス相を生成し、焼結体の高温特性を著しく劣化させるためである。さらに、市販の高純度アルミナ原料、高純度酸化ランタン原料を使用した場合にも一般に数十ppmのシリカが不純物として含まれており、これらの原料及び混合行程から混入するシリカ量を0.005重量%(50ppm)以下に低減することは困難である。そのため、混入するシリカ量をあらかじめ発光プラズマ分光分析法などにより定量し、配合時に添加するシリカ量を調節することが望ましい。

【0014】次に、上述のようにして得られた混合原料は、鋳込み成形、フィルタープレスなどの湿式成形により、あるいはスプレードライ法などにより一旦乾燥し、常法の乾式成形により生成形体に成形される。

【0015】次に、前記成形体は、常法の焼成方法、すなわち、まず空気中600~1000℃程度の温度で仮焼を行い、塩類、分散剤、混合行程で混入した樹脂等を加熱除去した後、1400~1800℃の温度、好ましくは1500~1700℃の温度で焼成することにより緻密化される。この際、高強度・高靱性を発現するために、相対密度97%以上に緻密化し、さらに、焼結体が $\text{Al}_2\text{O}_3$ と $\text{LaAl}_{11}\text{O}_{18}$ のみの結晶相となるまで原料間の反応を十分に進行させることが必要である。焼成温度が1400℃以下であれば、相対密度97%以上に緻密化できず、残存する気孔が破壊源となるため強度低下をもたらす。また、 $\text{LaAl}_{11}\text{O}_{18}$ 板状結晶が十分に生成しないため破壊靱性が低くなる。一方、焼成温度が1800℃以

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上では  $\text{Al}_2\text{O}_3$  及び  $\text{LaAlO}_3$  の過度の粒成長が生じ強度低下をもたらすので、上記温度範囲で焼成を行うことが必要である。さらに、焼成時間は、前記焼成温度に関連し、焼成温度が低いときは長く、また高いときには短くすることが好ましいが、上述の要件を満たし高強度・高靱性を発現させるためには、0.1~10時間の保持範囲内で緻密化することが推奨される。本焼結体は手法が容易である常圧焼成において緻密化されることを特徴とするが、ホットプレス、HIPにより緻密化を行うこともできる。

【0016】なお、焼成時の雰囲気としては、酸化雰囲気の方が好ましいが、非酸化雰囲気（例えば窒素ガスやアルゴンガス）あるいは真空中での焼成も可能である。

【0017】このようにして得られた本発明のアルミナ基焼結体は、板状粒子よりなるアルミナマトリックス中に板状ランタンβ-アルミナ粒子が分散した微構造を有する。そしてこのような板状粒子の絡み合った微構造により高靱性が発現され、さらにこのような異種板状粒子の分散により相互の異常粒成長が抑制され粒子の大きさの分布が均一となり高強度がもたらされ、焼結後低融点物質が残留しないため、高温強度発現を可能とした。したがって、本発明は従来では期待できなかった高強度、高靱性さらに高温での高強度を有するアルミナ基焼結体を得ることができる。

【0018】発明者らは、本発明に先立ち、アルミナに極微量の  $\text{SiO}_2$  のみを添加することにより、無添加では等軸状であった粒子が板状に成長することを見いだしている。しかし、 $\text{SiO}_2$  のみの添加では得られる焼結体は巨大なアルミナ板状粒子と微細なアルミナ板状粒子が混在した極めて不均質な組織を有し、それがため表の参考例に示されるように、強度、破壊靱性とも無添加のものよりもむしろ低くなることを確認している。また、前述のように  $\text{La}_2\text{O}_3$  単独の添加においても靱性向上レベルは低い。本発明の特徴は、このように  $\text{SiO}_2$ 、 $\text{La}_2\text{O}_3$  単独の添加ではなしえなかった高強度、高靱性化が  $\text{SiO}_2$  と  $\text{La}_2\text{O}_3$  の同時添加により達成されることにある。以下実施例に従って説明する。

【0019】

【実施例】所定量のテトラエチルシリケートに1N硝酸を250μl添加し、40℃で12時間攪拌することにより加水分解を行いシリカ分散液を作製した。蒸留水32ccにシリカ分散液の全量、所定量の  $\text{Al}_2\text{O}_3$  粉体および  $\text{LaAlO}_3$  粉体を入れ、さらに1N硝酸2.5ccを添加し、純度99.9%の高純度アルミナ製ボールと樹脂容器を用いて遊星ボールミルにより2時間混合を行った。

$\text{Al}_2\text{O}_3$  粉体として純度99.99%以上、粒径0.2μmのものを、 $\text{LaAlO}_3$  粉体は純度99.9%以上、粒径

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0.5μmのものを使用した。配合重量は約70gであり、配合は表に示す14種類の組成について行った（本発明以外の参考例を含む）。このようにして得られたスラリーを4kg/cm<sup>2</sup>の圧力下で鋳込み成形を行い、60×50×7mmの大きさの成形体を得た。温度50℃、湿度50%の恒温・恒温乾燥器で24時間乾燥させた後、塩類および混合容器からの混入樹脂を除去するため、空气中で800℃、1時間仮焼を行った。この仮焼体をアルミナルツボに設置し、空气中で10℃/min.の昇温速度で1600℃まで加熱し、1600℃で2時間保持を行い焼結体を得た。得られた焼結体は3×4×40mmの試験片に切断、研削を行った後、JIS R-1601による室温4点曲げ強度測定、JIS R-1604による1200℃での高温4点曲げ強度測定、及びJIS R-1607のSEPB法による破壊靱性測定を行った。さらに、配合物の混合、成形、焼成工程における不純物、特にシリカの混入を考慮して、焼結体の化学組成を発光プラズマ分光分析（ICP法）により求めた。なお、ICP法による化学分析において、Al、La、Si以外の陽イオン不純物は検出されなかった。これらの機械的特性、分析組成さらに密度測定、X線回折による結晶相の同定結果も配合組成と合わせて表に示す。尚、表中の密度は理論密度を基礎とする相対密度（%）で示してある。

【0020】

【発明の効果】表から明らかなように、本発明の組成範囲内においては、得られた焼結体は、結晶相が  $\text{Al}_2\text{O}_3$  と  $\text{LaAlO}_3$  からなり、常温強度が500 MPa以上、高温（1200℃）強度が350 MPa以上、かつ破壊靱性が5 MPa·m<sup>1/2</sup>以上を有する。

【0021】以上述べたように本発明によれば、従来のアルミナ基セラミックスでは期待できなかった高強度、高温高強度並びに高靱性の同時発現が可能なアルミナ基セラミックスを提供することができる。

【0022】従って、本発明によるアルミナ基セラミックスを用いることにより、既存の材料では対応が困難であった腐食環境下における構造材料として、また耐熱合金や非酸化物セラミックス材料に代わる安価な高温構造材料等として幅広い用途が期待される。具体的には耐食性・耐摩耗性を利用した軸受け、ポンプ、シール、ノズル、ベアリング等機械部品、さらに耐熱性の観点からは熱交換器、エンジン、ガスタービン部品などの利用が考えられる。また、従来の電子材料部品、パイオセラミックス等機能性材料の分野においても靱性改善による材料の信頼性の飛躍的な向上が期待される。

【表1】

| 試料    | 原料粉末の配合組成                        |                                  |                         |                                  | 焼結体の分析組成                         |                         |      | 相対密度 (%) | 抗折強度(MPa) |        | 破壊靱性<br>( $\text{MPa}\cdot\text{m}^{1/2}$ ) | 構成結晶相   |
|-------|----------------------------------|----------------------------------|-------------------------|----------------------------------|----------------------------------|-------------------------|------|----------|-----------|--------|---|---|
|       | $\text{Al}_2\text{O}_3$<br>(wt%) | $\text{La}_2\text{O}_3$<br>(wt%) | $\text{SiO}_2$<br>(ppm) | $\text{Al}_2\text{O}_3$<br>(wt%) | $\text{La}_2\text{O}_3$<br>(wt%) | $\text{SiO}_2$<br>(ppm) | 密度   |          | 室温        | 1200°C |   |   |
| 実施例 1 | 99.0                             | 1.0                              | 40                      | 99.0                             | 1.0                              | 105                     | 99.1 |          | 550       | 370    | 5.0   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " 2   | 99.0                             | 1.0                              | 920                     | 98.9                             | 1.0                              | 985                     | 99.0 |          | 530       | 360    | 5.5   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " 3   | 97.7                             | 2.3                              | 330                     | 97.7                             | 2.3                              | 400                     | 99.3 |          | 570       | 390    | 5.3   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " 4   | 95.4                             | 4.6                              | 530                     | 95.3                             | 4.6                              | 600                     | 99.2 |          | 870       | 440    | 5.4   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " 5   | 93.2                             | 6.8                              | 530                     | 93.1                             | 6.8                              | 608                     | 99.0 |          | 640       | 410    | 5.2   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " 6   | 90.1                             | 9.9                              | 50                      | 90.1                             | 9.9                              | 110                     | 98.0 |          | 550       | 380    | 5.0   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " 7   | 90.1                             | 9.9                              | 930                     | 90.0                             | 9.9                              | 990                     | 97.2 |          | 510       | 350    | 5.7   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| 参考例 a | 100                              | 0                                | 0                       | 100                              | 0                                | 56                      | 98.9 |          | 470       | 290    | 3.6   | $\text{Al}_2\text{O}_3$                                   |
| " b   | 100                              | 0                                | 600                     | 99.9                             | 0                                | 670                     | 98.1 |          | 360       | 280    | 3.5   | $\text{Al}_2\text{O}_3$                                   |
| " c   | 100                              | 0                                | 850                     | 99.9                             | 0                                | 937                     | 98.8 |          | 410       | 270    | 3.8   | $\text{Al}_2\text{O}_3$                                   |
| " d   | 99.2                             | 6.8                              | 0                       | 99.2                             | 6.8                              | 80                      | 99.3 |          | 610       | 420    | 4.3   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " e   | 95.4                             | 4.6                              | 1410                    | 95.2                             | 4.6                              | 1500                    | 99.1 |          | 470       | 260    | 5.8   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " f   | 88.6                             | 11.4                             | 400                     | 88.5                             | 11.4                             | 505                     | 97.3 |          | 490       | 340    | 5.2   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |
| " g   | 88.6                             | 11.4                             | 1390                    | 88.4                             | 11.4                             | 1510                    | 98.2 |          | 470       | 280    | 5.8   | $\text{Al}_2\text{O}_3$ , $\text{LaAl}_{11}\text{O}_{19}$ |